PHENOMENA DEPENDING ON THE CHANGE OF ELASTIC FREQUENCIES IN SOLID BODIES WITH PRESSURE

By F. Zwicky*

Abstract

Shift with pressure of the residual rays of a crystal.—Born's theory of the constituent forces in heteropolar crystals is adopted. As a new conclusion of this theory a formula for the shift of frequencies of residual rays with pressure is deduced. The shift corresponding to a pressure of 10,000 atm. amounts approximately to 7μ in the case of NaCl (residual rays at 50μ).

Effect of pressure on the electrical conductivity of metals.—Qualitative conclusions are drawn with respect to the dependence of elastic frequencies on pressure in any crystal. This leads to a rational explanation (suggested at first by Grüneisen) for the effect of pressure on the specific electric conductivity of metals, this conductivity being in general increased by pressure. The relation of our results to those obtained by Grüneisen and Bridgman previously in a quite different way, is discussed.

1. Introduction

THIS investigation was at first concerned with the problem of determining the shift of frequency of residual rays with pressure. It dealt naturally with heteropolar substances only, as only crystals built up by ions show selective frequencies in the far infra-red. From the results, however, it could be seen that it is possible to draw some important conclusions with regard to the conductivity of metals.

We first give the derivation for the change of frequency ν of residual rays with pressure P. The actual computation will be carried through only for the simple case of a cubic lattice of the type NaCl. The extension of the calculations to more complicated types of crystals would not involve any particular difficulties. Cases in which different tensions are applied in different directions of the crystal could also be calculated in the same way as described in this paper.

From the work of Born, Kossel and others it is known, that the cohesive forces in heteropolar chemical compounds are mainly of electrostatic origin, resulting from the electric field produced by the different ions. This theory has proved to possess a considerable range of validity, as lattice constants, compressibilities, elastic constants, frequencies of residual rays and heats of sublimation can be calculated from it. The results of such computations are in good agreement with the experimental data. The only very serious discrepancy between the theory and the facts seemed to appear between the calculated values of the breaking stress and the observed ones. The theoretical breaking stress, as deduced by the author,[1] was 400 times greater than

* Research Fellow in Physics, International Education Board.

the measured values known at that time. But also in this case the theory was proven to be right by the careful investigations of A. Joffé and his school.[2] Joffé showed that in all the previous experiments much too low values for the breaking stress had been found because of imperfect surfaces of the crystals used (tiny cracks). Eliminating this source of error Joffé found values for the breaking stress approaching very nearly those predicted by the calculations.

Born's theory was extended by different investigators,[3] who have taken into account the deformability of the ions in an electric field. In addition to this the repulsion forces were taken more exactly into consideration. These are necessary to secure the stability of the lattices. No real explanation has yet been found as to their true origin. A satisfactory treatment, however, of all the phenomena mentioned above could be given by assuming these forces to be inversely proportional to some high power of the mutual distance r_{ik} of two ions i and k. The two particles then, carrying charges e_i and e_k respectively, possess the mutual potential energy

$$\epsilon_{ik}=e_ie_k/r_{ik}+A_{ik}/r_{ik}^{p_{ik}} \tag{1}$$

The constants A_{ik} and p_{ik} are to be determined. Three points of view have been adopted with regard to these constants. At first, attempts were made by Born and Landé to deduce the exact values for them in a rational way, with the help of atomic models. But no consistent results could be obtained because of lack of knowledge of the fundamental quantum laws governing the mutual interaction of two atomic systems.

The second procedure consists in the deduction of A and p from the behaviour of gas atoms similar to the ions in question. From viscosity measurements in argon, for instance, the repelling force acting between two argon atoms can be determined.[4] A slight extrapolation permits one to apply the same law of force for the interaction of two Cl^- ions or of two K^+ ions, because of the fact that these ions have very similar electronic structure to the neutral A-atom. In this way the different properties of the alkali-halide crystals could be deduced.

The third method was originally applied by Born,[5] who used the experimental data of the lattice constant and of the compressibility to determine A_{ik} and p_{ik} in every special case. The other properties of the crystals may then be calculated with the help of the A and p thus obtained. We choose this simple point of view as our starting point.

[1] F. Zwicky, Physik. Zeits. **24,** 131 (1923).

[2] A. Joffé and M. Lewitzki, Zeits. f. Physik, **35,** 442 (1926).

[3] See for instance M. Born, Die Atomtheorie des festen Zustandes, Enzyklopaedie der math. Wissenschaften, Vol. V_3, Heft 4. All references made in our paper to previous work on heteropolar crystals may be found summarized in this book.

[4] J. E. Lennard-Jones, Proc. Royal Soc. London, **109,** 584 (1925).
J. E. Lennard-Jones and P. A. Taylor, Proc. Royal Soc., **109,** 476 (1925).

[5] Ref. 3, p. 733.

Assuming for the mutual potential energy of two ions the expression (1) we get for the energy contained in a crystal of the type NaCl the amount (per ion).[6]

$$\epsilon = \sum_k \epsilon_{ik} = -13.9e^2/a^4 + \alpha' A/a^p \tag{2}$$

a = lattice constant, α' = some function of p.[6] The sum has to be taken over all the particles surrounding the ion i. For numerical computations see Ref. 3.

The condition necessary for the equilibrium of the crystal is

$$(\partial\epsilon/\partial a)_{a=a_0} = 0 \tag{3}$$

or

$$1.74e^2 - \alpha A/a_0{}^{p-1} = 0 \tag{4}$$

which means a relation between A and p, provided that the lattice constant a_0 is taken from the experiments.

Deducing on the same basis a formula for the compressibility and comparing it with the observed data, Born was able to determine A and p seperately. It is found that p is approximately equal to 8 or 9. For different crystals one finds slightly different values varying from 7.5 to 9.5. Numerical computations then give α for different values of p as in the following table.

TABLE I

p	7.5	8	8.5	9
α	4850	7200	10380	15200

2. RESIDUAL RAYS

It has been shown by previous authors[7] that the origin of the selective absorption and reflection of radiation in the far infra-red by heteropolar crystals is connected with the oscillations which the positively charged part of the lattice is able to perform relative to the negatively charged part. These oscillations will indeed be excited by incoming electromagnetic radiation, as the electromagnetic field connected with this radiation will force the charges of different sign in opposite directions. Resonance occurs when the incoming and the elastic oscillations have approximately the same frequency. It is easy to show that crystals of the NaCl type possess only one characteristic oscillation of the kind mentioned. Our task is to calculate its frequency in the case of uniformly applied external pressure. For this purpose we have to determine the force which is necessary to hold the positive and the negative partial lattices in relative displacement $\xi^+ - \xi^- = \xi$ (see Fig. 1.). We will obtain this force by deriving first the change in potential energy $\Delta\epsilon$ of a particle due to the displacement ξ.

The effect of the displaced electric charges may be obtained by making use of the expression for the Lorentz force in a polarized isotropic medium.

[6] A_{ik} and p_{ik} in (1) are really dependent on the individual ions i and k. It has been shown however that the effect produced by their differences is a very small one and can be neglected in the first appoximation.

[7] Ref. 3, p. 740.

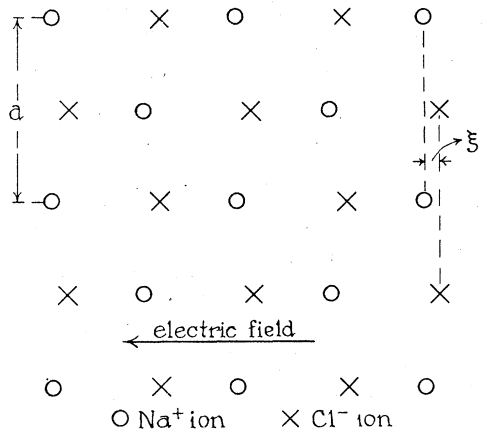

Fig. 1

The electric polarization or the moment per unit volume M being in our case equal to

$$M=\tfrac{1}{2}Ne\xi \tag{5}$$

(N = number of ions per cm^3)

The force per ion, due to the polarization is

$$4\pi eM/3=2\pi Ne^2\xi/3 \tag{6}$$

For the work necessary to produce a displacement $\delta\xi$ we then get

$$\delta\epsilon^-=-2\pi Ne^2\xi\delta\xi/3 \tag{7}$$

By integration we obtain

$$\Delta\epsilon^-=-\pi Ne^2\xi^2/3 \tag{8}$$

$\Delta\epsilon^-$ is a negative quantity as can easily be seen. We transform our formula by making use of the fact that there are eight particles contained in the elementary volume a^3.

$$\Delta\epsilon^-=-\pi Na^3e^2\xi^2/3a^3=-8\pi e^2\xi^2/3a^3 \tag{9}$$

The member $\Delta\epsilon^+$ originating from the repelling forces is obtained by adding the contributions of all the single ions surrounding the one considered. As a result,

$$\Delta\epsilon^+=\beta A\xi^2/a^{p+2} \tag{10}$$

where

$$\beta=4p(p-1)\left[2^p+4(2/3^{1/2})^p/9+4(2/5^{1/2})^p/5+\cdots\right]$$

Numerical values of β for some values of p are reproduced in table II.

TABLE II

p	7.5	8	8.5	9	9.5
β	35600	57700	92800	148000	235000

The whole energy due to the displacement ξ of the lattices is therefore

$$\Delta\epsilon=\Delta\epsilon^{-}+\Delta\epsilon^{+}=(-8.4e^2/a^3+\beta A/a^{p+2})\xi^2 \tag{11}$$

From this we get the force K per ion by differentiation

$$K=\partial(\Delta\epsilon)/\partial\xi=2[-8.4e^2/a^3+\beta A/a^{p+2}]\xi=f\xi \tag{12}$$

Now the equations of motion for the two different ions are

$$\begin{aligned} m^{+}d^2\xi^{+}/dt^2&=f(\xi^{-}-\xi^{+})=-f\xi \\ m^{-}d^2\xi^{-}/dt^2&=f(\xi^{+}-\xi^{-})=f\xi \end{aligned} \tag{13}$$

Combining these equations we obtain

$$d^2\xi/dt^2=-f\xi(m^{+}+m^{-})/m^{+}m^{-} \tag{14}$$

The harmonic oscillations representing the solution of this equation are characterized by the frequency

$$\nu=[f(m^{+}+m^{-})/m^{+}m^{-}]^{1/2}/2\pi \tag{15}$$

Denoting this frequency by ν_0 in case no external pressure is applied we have

$$\nu_0=[(-8.4e^2/a_0{}^3+\beta A a_0{}^{p+2})(m^{+}+m^{-})/2m^{+}m^{-}]^{1/2}/\pi \tag{16}$$

Making use of the relation (4) this may be written as

$$\nu_0=[(-8.4+1.74\beta/\alpha)e^2(m^{+}+m^{-})/2m^{+}m^{-}a_0{}^3]^{1/2}/\pi \tag{17}$$

Application of external pressure changes the lattice constant from a_0 to $a_0+\delta$, where δ is to be considered as a small quantity in all practical cases. Developing to the first order in δ we obtain

$$\nu=\nu_0(1-\gamma\delta/a_0) \tag{18}$$

where

$$\gamma=[3\cdot 8.4-1.74\beta/\alpha(p+2)]/2(-8.4+1.74\beta/\alpha)$$

Evaluating γ numerically the following table can be established

TABLE III

p	7.5	8	8.5	9
γ	11.2	10.5	9.9	9.5

From this it may be concluded that the frequency changes relatively much more rapidly with pressure P than does the lattice constant. Expressing δ with the help of the volume-compressibility κ we get

$$\begin{aligned} \delta&=-\kappa a_0 P/3 \\ \nu&=\nu_0(1+\gamma\kappa P/3) \end{aligned} \tag{19}$$

As an application we shall give the actual figures in the case of rock salt. For NaCl the compressibility found in the experiment is (P measured in Kg per cm^2)

$$\kappa=4.14\cdot 10^{-6}$$

So to a pressure of 10000 atm. there would correspond the following frequency (for p the value 8 is used as given by Born's calculations)

$$\nu=\nu_0(1+0.145)$$

This means a displacement of the selective absorption line from $\lambda=50\mu$ to $\lambda=43.6\mu$. Pressures of this order can be realized experimentally either directly in some mechanical way (Bridgman) or by some indirect method, as for instance by electrolysis of the crystals. Joffé[8] has shown that extremely high pressures can be reached in this latter way because of the enormous forces the space charges in the lattice exert on each other. So the possibility exists of checking our formula experimentally. As I hear through the kindness of Professor Joffé, measurements of this kind are going on in the Polytechnical Institute at Leningrad. The results thus obtained will be of some importance for the theory of crystals because they supply a new means of getting more information about the nature of the repelling forces. These are not yet very well known.

3. Resistance of Metals Under Pressure

The specific electric resistance of metals in general decreases with pressure. This has been shown especially by Bridgman[9] in a long series of beautiful experiments. Now this fact presents considerable difficulty to the classical theories of metallic conduction. In fact we can deduce from these theories an approximate relation of the following type

$$1/\rho \propto N_e\Lambda$$

where $\rho=1/\sigma$ is the specific resistance, N_e the number of free electrons per cm^3 and Λ the mean free path for these electrons. Now Λ, being inversely proportional to the number of atoms N_a per cm^3, ρ will be roughly independent of the pressure in case we assume that N_e increases in the same way as N_a. More rigorous calculations show that the resistance should increase under all circumstances with pressure, which is in strict contradiction with the facts. Now there has been advanced an explanation of this fact by Grüneisen.[10] The underlying idea is essentially this. The mean free path of electrons in the metal is not independent of temperature for the reason that the thermal oscillations of the atoms disturb their motion.[11] This may be thought to happen in the following way. In the space lattice of the metal the electrons of long path, moving approximately parallel to one of the lattice planes, contribute most to the conductivity. Now these electrons are more and more disturbed in their motion as the atoms are more and more displaced by the thermal agitation. The mean free path will then be approximately

$$\Lambda \propto 1/d^2$$

[8] My information is taken from Joffé's lectures at the Calif. Inst. of Technology, 1925.

[9] See for instance P. W. Bridgman, American Acad. of Arts and Sciences. Several papers in 1922–1925.

[10] E. Grüneisen, Verh. d. D. Phys. Ges. **15**, 186 (1913). I am indebted for this reference to the Editors of the Physical Review.

where d is now the mean amplitude of the atom in its thermal agitation. From this standpoint we have the possibility of accounting for the experimental variation of conductivity with temperature[12] without being in contradiction with the facts of specific heat and the pulling of electrons from cold wires (electric field currents).[13] Furthermore the increase of specific conductivity with pressure can easily be explained on this basis without making use of any artificial assumptions. Indeed the amplitudes of the atoms in their motion of thermal agitation are determined by the strength of the elastic force (f dynes per cm displacement are pulling the atoms back to their average positions). Now this elastic force can be compared with that mentioned above in the case of heteropolar crystals. We then make use of the results obtained in Section 2, and assume that they are approximately right for homopolar crystals also, i.e. that they have the same dependence on pressure as far as the magnitude is concerned. This could be justified indeed in a general way by merely making use of the fact that the repelling forces vanish much more rapidly with increasing distance of the particles under consideration than the attractive forces, which will be nearly always the case. If then d be the average maximum displacement of an atom we shall have for high temperatures this relation

$$fd^2 = 3kT \qquad (k = 1.37 \times 10^{-16}\text{erg})$$

Denoting with f, d and f_0, d_0 the elastic constant and the amplitude of the atom in the compressed and in the natural state of the crystal respectively, then

$$d^2/d_0^2 = f_0/f = \nu_0^2/\nu^2 = (1 - 2\gamma\kappa P/3)$$

$$\sigma \propto \Lambda \propto 1/d^2 \propto (1 + 2\gamma\kappa P/3)$$

$$\sigma = \sigma_0(1 + 2\gamma\kappa P/3) \tag{20}$$

Thus from this point of view the increase of specific electrical conductivity σ with pressure is explained as follows. Since the elastic bonds of the atoms in the crystal increase in strength very rapidly with pressure, it is seen that the areas covered by the atoms in their thermal agitation decrease with pressure much more rapidly than the whole volume under consideration. For this reason the free space between the atoms (counted per cm^2) increases with pressure, so as to allow the conductivity electrons to move on longer mean free paths than before.

Experimentally it is found that

$$\sigma = \sigma_0(1 + cP) \tag{21}$$

[11] This conception has been adopted by different theories of metallic conduction. See for instance R. Seeliger, Enzyklopaedie d. math. Wissenschaften, Teubner 1922, Vol. V_2, Heft 5, p. 870.

[12] Assuming Λ constant, the classical theory gave $\sigma \propto T^{-\frac{1}{2}}$ instead of $\sigma \propto T^{-1}$.

[13] R. A. Millikan and C. F. Eyring, Phys. Rev. **27**, 51 (1926).

So that for a lattice of the type NaCl, comparing (20 with 21) we should predict the following relation between the pressure coefficient c of electric conductivity and the compressibility κ

$$c = 2\gamma/3\kappa \sim 7\kappa \tag{22}$$

Now for metals we shall not have exactly the same molecular forces acting as in NaCl. Still our formula should give the right order of magnitude for the coefficient c, since its derivation is based essentially only on the fact that the repelling forces, compared with the attractive forces, decrease very rapidly with distance. Some experimental data obtained by Bridgman are collected just at random in Table IV, to show that our conclusion is right.[14]

TABLE IV

	Fe	Co	Rh	Pd	Ir	Pt	Au
$c\times10^7$	24.2	9.3	17.4	19.6	13.5	19.5	33.3
$\kappa\times10^7$	5.87	5.39	3.72	5.2	2.7	3.6	4.8
c/κ	4.1	1.7	4.65	3.75	5	5.4	6.9

There are also some metals, as for instance Bi, Sb, Ca, Li and Sr which behave abnormally. Their specific resistance increases with pressure. Evidently such a treatment as that suggested in this paper cannot be complete. It does not take into account such individual properties of the different metals as the dependence of number of free electrons on pressure, the forces acting on electrons in the interior of the crystals, etc.

In Grüneisen's original paper the change of elastic frequency with pressure has been computed in a quite different way from ours. He makes use of the quantum theory of equation of state of solid bodies (Debye, Grüneisen). Grüneisen's method is mainly a phenomenological one. This involves the necessity of making some general assumptions as to the behavior of solid bodies with temperature. It is, however, interesting to see that the results thus obtained check in the order of magnitude with those obtained in this paper in a more direct way. This is a justification of Grüneisen's assumptions.

Bridgman[15] in his gap theory of metallic conduction also deduces the effect of pressure on conductivity by making use of the fact that the elastic frequencies decrease with pressure. His final formula for the change of conductivity is essentially the same as we have used it. His underlying picture, however, is quite different from that given above insofar as the electrons do not move freely through the spaces between the atoms. They on the contrary do not meet any resistance in moving through the atoms. It appears, however, to the writer that this theory is based too much on an overestimation of the size of the atoms in a crystal. Bridgman indeed considers them in general to be in direct mutual contact at the absolute zero point. Now most of the known evidence seems to indicate that there are large free spacings between the atoms. Such evidence is for instance

[14] P. W. Bridgman, Proc. Amer. Acad. of Arts and Sciences, Vol. 59, No. 5, p. 114.
[15] P. W. Bridgman, Phys. Rev. **9**, 269 (1917); **17**, 161 (1921); **19**, 114 (1922).

furnished by the direct determination of atomic radii in crystals by investigation with x-rays. Scherrer and Debye[16] find for instance in the case of diamond that the diameter of a C-atom (volume actually covered by the revolving electrons) amounts only to one-fourth of the mutual distance of the atoms. A second method of determining the gaps consists in direct comparison of diameters known from the kinetic theory with measured lattice constants. This gives in the case of alkali-halides dimensions of the gaps comparable with the dimensions of the constituting ions. Very strong evidence in favor of large gaps seems furthermore to be indicated by the fact that large amounts of matter may be transported through crystals without disturbing the lattice (electrolysis through crystals). The fact that constituent atoms may be extracted from crystals (mica for instance)without destroying the crystals, points also in the same direction.

It would be of very great importance if some conclusive evidence could be found with regard to the question whether slow electrons pass through atoms in approximately straight lines or not. Many physicists seem to consider, for instance, Ramsauer's well known results on behavior of slow moving electrons in certain gases as such evidence.[17] The writer[18] has tried to show, however, that even from the standpoint of classical dynamics it is not necessary to draw this conclusion. It would be, however, of extreme interest for the modern development of the quantum theory if this question could be settled definitely by some new experiments.

As another phenomenon connected with the change of elastic frequencies with pressure we may mention the specific heat of solid bodies. It is obvious that from the point of view of the quantum theory this change will affect the characteristic temperature Θ (Debye). Increase of ν means a higher value for Θ. The abnormal behavior (drop of specific heat) should be found then at higher temperatures in case external pressure is applied.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
January 18, 1927.

[16] P. Scherrer and P. Debye, Physik. Zeits., Vol. 19, p. 474 (1918).

[17] C. Ramsauer, Ann. d. Physik. Vol. **64**, p. 513, 1921. "Slow" electrons means that their energy is less or about equal to the resonance energy of the deflecting atoms. The free electrons moving in the electric field in the metal will probably be such. Ramsauer's result is, that for several atoms as A, Kr, and Xe the effective area in their interaction with slow electrons is much smaller than the area given by the kinetic theory of gases. Electrons with their initial line of motion pointing towards the atom may in this case continue their path without being deflected appreciably by the atoms.

[18] F. Zwicky, Phys. Zeits. **24**, 171 (1923).